(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 418 015 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 90309876.2

(51) Int. Cl.5: D21H 17/17, D21H 17/23

(22) Date of filing: 10.09.90

(30) Priority: 11.09.89 GB 8920456

(43) Date of publication of application:
20.03.91 Bulletin 91/12

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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(54) Active sizing compositions.

(57) The compositions comprise an aqueous emulsion containing a ketene dimer reactive sizing agent and an anionic dispersant or emulsifier such as sodium lignosulphonate, calcium lignosulphonate or the sodium salt of naphthalene sulphonic acid. In addition an extender or modifier such as an anionic polyacrylamide, an anionic starch or colloid silica can be present to extend or modify the anionic charge density of the composition. The compositions are particularly effective in sizing systems containing cationically charged fillers, or cationic additives such as certain retention aids and fluorescent whitening agents.

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ACTIVE SIZING COMPOSITIONS

This invention relates to active sizes containing a reactive sizing agent and a dispersant.

For convenience, the term "paper" is used in this specification to mean any form of paper, paperboard and related products, the manufacture of which involves the action of a sizing agent upon cellulosic or other fibres.

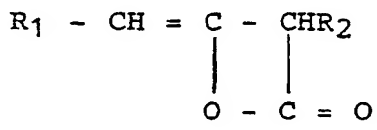
Traditionally, paper has been sized with rosin in conjunction with alum, which acts as a precipitant. More recently, reactive sizes have been introduced, in which a sizing agent reacts directly with the cellulose of the paper. One class of reactive sizes in common use is the ketene dimer sizes. These are typically used as emulsions in water in conjunction with dispersants and emulsifiers, which serve to stabilise the emulsion.

Previous ketene dimer sizes have contained, as dispersant, cationic components such as starches, polyamines, polyamides and polyacrylamides. These emulsifiers and dispersants are homogenised in situ with the ketene dimer to form cationically stabilised emulsions.

Whilst satisfactory in many applications, the known cationically stabilised ketene dimer sizes give rise to problems in certain applications. In particular, certain grades of paper for liquid packaging and the manufacture of photographic papers involve, in their manufacture, the use of large quantities of cationic polyamide amine epichlorohydrin resin, in order to produce favourable wet-strength properties in the finished paper. In a wet-end process, the resin is normally added to the thickstock. The resin has a high substantivity to cellulose, in order to produce sufficient coverage of the fibre. The introduction of further cationic components, such as starch, dry-strength resin and cationically stabilised ketene dimer size can lead to poor retention of the components by the cellulose and result in slow drainage, poor strength properties and low sizing efficiency.

Problems can also arise in surface sizing processes, particularly because the trend in the manufacture of fine speciality papers is to apply the cationic starch-stabilised ketene dimer size to the surface of the paper sheet in conjunction with a fluorescent whitening agent (FWA). Such agents are usually anionic in nature and their use in conjunction with cationic-stabilised sizes can lead to a reduction in the effectiveness of the FWA and cause a quenching effect which gives rise to a yellower paper.

The present invention provides an active sizing composition which comprises an aqueous emulsion of a reactive sizing agent and an anionic dispersant and/or emulsifier serving to stabilise the emulsion, the reactive sizing agent comprising at least one compound according to the formula



wherein R_1 and R_2 are, independently of each other, hydrocarbon radicals having at least six carbon atoms, more preferably alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkaryl radicals.

Sizing agents of the invention can offer advantages especially in systems where cationic charged fillers e.g., precipitated calcium carbonates are present or in systems using cationic components e.g., retention aids of polyacrylamide, polyamine, PEI, etc. in furnishes consisting of groundwood, thermomechanical pulps or chemical thermomechanical pulps where limited hydroxyl (OH^-) sites are available for AKD attachment and reactivity.

The compositions of the invention are particularly suitable for use as an internal size in sizing operations carried out at the wet end of a paper-making process.

In particularly preferred sizing agents, R_1 and R_2 are, independently of each other, C_{12} to C_{22} alkyl groups, C_{14} to C_{19} alkyl groups being especially preferred. The compounds in which R_1 and R_2 are each $C_{14}H_{29}$ or $C_{16}H_{33}$ are most highly preferred and are referred to hereinafter as "palmitic-stearic dimer". The latter compounds can be regarded as the cycloaddition products of one ketene molecule of the formula R_1-CH=C=O and one ketene molecule of the formula R_2-CH=C=O, wherein R_1 and R_2 are each $C_{14}H_{29}$ or $C_{15}H_{35}$.

It has surprisingly been found that, contrary to expectations, active sizing compositions according to the invention can be effective in their sizing properties, particularly when used in highly-cationic environments, such as those encountered in wet-end sizing in the manufacture of liquid packaging papers and photographic papers as mentioned above, and those, also mentioned above, when the active size is used in connection with fluorescent whitening agents. In addition, papers using cationic fillers such as precipitated

calcium carbonate can be sized efficiently using an anionically charged alkyl ketene dimer size of the present invention. That the compositions of the invention can be effective sizing agents is the more surprising because it has previously been supposed in the art that an anionically stabilised sizing agent would lack the necessary affinity with the hydroxyl groups of the cellulose and that a cationically stabilised emulsion was necessary to provide the necessary retention of the sizing agent by reaction with the hydroxyl groups.

The dispersant and/or emulsifier stabilising the emulsion can be any suitable anionic dispersant or emulsifier. Sodium lignosulphonate, calcium lignosulphonate and the sodium salt of naphthalene sulphonic acid, and mixtures thereof, are examples of suitable dispersants. The dispersant and/or emulsifier is preferably used in a total amount of 0.5% to 10% based on the weight of the reactive sizing agent, the actual amount used in any particular composition being that which imparts a desired anionic charge to the dispersed sizing agent.

If desired, the anionic charge density in the sizing compositions of the invention can be extended or modified using components such as anionic polyacrylamides, anionic starch or colloidal silica as emulsifiers. The sizing agent is preferably present in the sizing composition in an amount of 5% to 20% by weight, more preferably 10% to 15% by weight, of the sizing composition.

The sizing compositions, if desired, may be used in conjunction with effective quantities of material such as retention aids, dry strength agents and drainage aids, for example alum which acts both as a drainage aid and as a scavenger for anionic colloidal debris.

The sizing compositions of the invention can be made by any convenient process, but preferably are made by homogenising the reactive sizing agent in liquid form (if necessary after heating to melt the material) with the dispersant and/or emulsifier and the appropriate amount of water to form an aqueous emulsion. For example, the dispersant and/or emulsifier is dissolved in water at 65 to 80 °C to which is added molten ketene dimer premelted at 65 to 80 °C. The resultant mix is homogenised at 2500 to 3500 psi to form a stable emulsion.

The invention will now be described further by way of examples.

EXAMPLES 1 to 4 and COMPARISON EXAMPLES 5 to 10

In the experimental work which is described hereafter, all sizing tests were carried out on a 50:50 dry weight mixture of bleached HW and SW kraft pulp which had been simultaneously beaten to a 40 °SP endpoint in an experimental-scale valley beater. The sizing test employed was a 16 hour, 1.0% w/v lactic acid edgewick test.

Sample preparation without recirculation.

1000cm^3 of 1.0% consistency stock was placed in a 1500cm^3 beaker, to which the necessary amounts of chemicals (see Table 2) were added sequentially at 30-second intervals using plastics syringes with an accuracy of ±0.1cm^3. The 30-second interval was extended to 60 seconds after addition of the Kymene 557. The pH of the mixture was adjusted to 7.5 by addition of sodium bicarbonate immediately after addition of the Kymene 557. Mixing of the components was accomplished with a mechanical stirrer operated at 100 rpm. Sheets were produced from the final mixture in a British Standard handsheet mould and pressed in a pneumatically operated Voith handsheet press for 5 minutes at a pressure of 50 psig (345 k Pa). The sheets were then dried by passing them four times around a photographic drum dyer operated at 105 °C, giving a residence time of 3.3 minutes, followed by 5.0 minutes in a forced-draught oven at 105 °C. After cooling for at least 10 minutes, the sheets were roughly cut, laminated and finely cut to a final size of 5.0 cm x 12.5 cm.

Sample preparation with recirculation.

3500cm^3 of 2.79% consistency stock was placed in a ten-litre pail. Both Kymene 557 and AKD size were then added to this suspension. The pH was adjusted to 7.5 by addition of sodium bicarbonate. Next, sufficient of this "thickstock" to contain 10g of dry fibre was diluted to a total volume of 1000cm^3. This resulted in a "thinstock" having a consistency of 1.03%. Next, alum, Accostrength 85 and Staklok 400 were added to the thinstock. This thinned suspension was drained through a Messmer consistency apparatus.

The retained solid was discarded and the filtrate was then used to dilute more of the thickstock, so that further additions of alum, Accostrength 85 and Staklok 400 could be made. This cycle of dilution, drainage and addition of alum, Accostrength 85 and Staklok 400 was repeated until it had been carried out nine times before handsheet manufacture. Just prior to sheet formation, the pH was again adjusted to 7.5 by addition of further sodium bicarbonate. Thorough mixing of the components was accomplished manually. Sheets were produced as described above.

Sample Testing:

All samples were weighed and then placed 2.5cm below the surface of a 1.0% w/v lactic acid solution. After 16 hours, the samples were removed, dried and reweighed. The results are shown in Table 1.

TABLE 1

Example	Dispersant	Sample Preparation	Fluid Pick-up (g)
1	Keydime SP1	S1	0.3860
2	Keydime SP1	S2	0.4013
3	Keydime SP1	S3	0.4299
4	Keydime SP1	S1-R	0.32
5	Keydime D10	S1	0.3612
6	Keydime D10	S2	0.4088
7	Keydime D10	S3	0.4330
8	Keydime D10	S1-R	0.32
9	Keydime D125	S2	0.4102
10	Keydime D125	S3	0.4191

Examples 5 to 10 are comparison examples employing cationically-stabilised AKD sizing agents.

The codes S1, S2, S3 and S1-R describe the sample preparation techniques used:

Keydime SP1 is a dispersant containing sodium lignosulphonate and the sodium salt of naphthalene sulphonic acid. It is available from Albright & Wilson Limited. Keydime D10 and Keydime D125 are cationically stabilised AKD sizing agents containing, on a dry weight basis, 10% AKD (the palmitic-stearic compound mentioned above) and, respectively, 2.5% and 1.25% cationic polymer. Keydime D10 and Keydime D125 are also available from Albright & Wilson Limited.

TABLE 2

Addition sequence

S1

(1) 8.0lb/T (4.0 kg/t) Kymene 557 (polyamide amine epichlorohydrin, available from Hercules Powder Co.)
(2) 7.0lb/T (3.5 kg/t) AKD (palmitic-stearic dimer)
(3) 1.0lb/T (0.5 kg/t) alum
(4) 4.0lb/T (2.0 kg/t) Accostrength 85 (an anionic dry strength agent comprising polyacrylamide dry polymer on dry fibre)
(5) 10.0lb/T (5.0 kg/t) Staklok 400 (cationic corn starch, available from Staley Manufacturing Co.)

S2

(1) 8.0lb/T (4.0 kg/t) Kymene 557
(2) 7.0lb/T (3.5 kg/t) AKD (as above)
(3) 1.0lb/T (0.5 kg/t) alum
(4) 10.0lb/T (5.0 kg/t) Staklok 400
(5) 4.0lb/T (2.0 kg/t) Accostrength 85

S3
(1) as S1
(2) 7.0lb/T (3.5 kg/t)AKD (as above) and 10.10lb/T (5.0 kg/t) Staklok 400, premixed
(3) 1.0lb/T (0.5 kg/t) alum
(4) 4.0lb/T (2.0 kg/t) Accostrength 85

S1-R as S1 but with recirculation

In each addition sequence, the AKD was added together with the Keydime SP1 (in examples 1 to 4) and as a component of the Keydime D10 or D125 (in examples 5 to 10), an AKD-Keydime SP1 emulsion having been formed by melting the AKD at 65 to 80 °C, dissolving the molten AKD in water at 65 to 80 °C and homogenising the mixture with Keydime SP_1 at 2500 to 3000 psi.

Examples 1 to 4, when compared with Examples 5 to 10, show fluid pick-ups (edgewick) with anionic agents comparable to or better than those of cationic agents. Examples 4 and 8 show that better results can be attained with recirculation which most realistically simulates the papermaking process.

EXAMPLES 11 to 15 and COMPARISON EXAMPLE 16

Edgwick evaluation tests consisting of two parts:
(1) Formation of sheets, and
(2) Coating and lactic acid tests were carried out on six further sizing compositions. The results are clearly indicative of the fact that anionic active sizing compositions perform well in the tests and are suitable for use in sizing papers for the liquid packaging industry.

Procedure

Stock used was 50/50 hardwood/softwood beaten to a Schopper Reiglar of 40°.

Chemical Additions

Thickstock:
3.2% A/R Wet strength resin (Kymene 557)
0.35% AKD/Fibre sizing composition

Thinstock
0.05% Dry Alum/Fibre
2 kg/t Accostrength 85
1% Dry Stalok 400

The procedure was followed for each of five sizing compositions having the following constituents:

Example 11
100g Ketene Dimer (palmitic-stearic)
1.25g Orotan (surfactant)
4.5g Wanin (surfactant)
800g Water

Example 12
100g Ketene Dimer (palmitic-stearic)
1.25g Orotan
4.5g Wanin
1.5g Percol 155 (50% solid Anionic Polyacrylamide)
800g Water

Example 13
100g Ketene Dimer (palmitic-stearic)
1.25g Orotan
4.5g Wanin
666g BMA (contains anionic silica) (15% solids)
133g Water

Example 14
100g Ketene Dimer (palmitic-stearic)
1.25g Orotan
4.5g Wanin
333g 1/2 BMA

166g Water
Example 15
100g Ketene Dimer (palmitic-stearic)
1.25g Orotan
4.5g Wanin
2.5g Lab 998 (ex Roquette) Anionic Starch
425g Water

After combination of the above materials, further water was added to adjust the compositions to an AKD solids content of 10% by weight.

The tests consisted of two parts:

Part 1:

250 gsm sheets were produced on laboratory sheet-forming apparatus and the consistency of the thinstock was 0.5%.

The sheets were dried at 105° C for 8 minutes then oven cured for 5 minutes.

Part 2:

Lactic acid immersion tests were carried out on the sheets. The sheets were coated with tape and cut to 12.5cm x 5cm strips. These strips were weighed before immersion in 2.5cm of 1% lactic acid for 16 hours. The strips were then reweighed and the pickup calculated in grams. The average of 3 results was taken for each sizing composition.

The edgewick tests gave the following results:

Example	Edgewick (g)	% Pickup
11	0.227	6.8
12	0.174	7.2
13	0.316	12.7
14	0.317	12.8
15	0.185	7.6
16	0.181	7.9

Example 16 is a comparison example using Keydime D10. These results overall indicate that anionic AKD sizing compositions perform as well if not slightly better than compositions in situations where high levels of cationicity are present. The compositions are therefore suitable for use in the liquid packaging industry.

EXAMPLES 17 to 19

A series of anionic size compositions were prepared and tested:

Composition	1	2	3
Additive/Dispersant:			
Naphthalene Sulphonic Acid	1.25	1.25	1.25
Na Lignosulphonate	4.5	4.5	4.5
Anionic Polyacrylamide	-	1.2	-
Colloidal Silica	-	-	37.5
Alkyl Ketene Dimer (Palmitic/Stearic)	100	100	100

All amounts are expressed as dry grams of material.

Emulsion Manufacture Procedure

In each case the process water was acidified prior to the addition of dispersants. The mixture was heated to 70° C before addition to a laboratory homogenizer which was preheated to the same temperature. Homogenization pressure was adjusted to 3500 psig (24 M Pa) (ideally 2500 to 5000 psig (17 to 34 M Pa)). Molten alkyl ketene dimer wax was added at 70° C and allowed three theoretical passes plus one to discharge. Upon discharge, the product was passed through a 200 mesh filter and the temperature rapidly reduced to below 20° C.

Laboratory Procedures

a) Stock Preparation

All work was performed on a 50:50 mixture of hardwood and softwood beaten in a Valley Beater to 40° SR (300 CSF).

b) Chemical Additives

Chemical additions were made using syringes having an accuracy of ± 0.1 cm^3. All chemical additives except precipitated calcium carbonate were diluted prior to use for accuracy of addition.

The precipitated calcium carbonate used for this work was a commercially available grade Albacar HO made at 20% solids with no dispersant added. Particle size averaged 2.7 microns with a Zeta potential of +5 mV.

c) Size Testing

The size test employed in this work was a 2-minutes Cobb test under standard conditions.

Results

Chemical Additions - lbs/ton dry basis on fibre

Example	Thickstock Starch	Filler	Size/Comp	Thinstock Retention Aid	2-Min. Cobb Off Dryer	Oven Cured	Sizing g/m^2 Natural Cured
17	10.0	300	3.0(1)	0.5	40	40	41
18	10.0	300	3.0(2)	0.5	36	36	37
19	10.0	300	3.0(3)	0.5	44	41	38

Starch-Stalok 400 Cationic Potato Starch commercially. available from Staley Starch Products Ltd.

Filler - Precipitated calcium carbonate - see above.

Size - Composition 1, 2 or 3 as above.

Retention Aid--Hydraid TRP-954. Cationic polyacrylamide commercially available from Calgon Ltd.

Machine Trial Data

Anionic size composition (1) of Example 11 was tested against a competitive, cationically stabilized size, Aquapal C348 supplied commercially by Hercules Powder Co. Sizing was measured to a standard 1-min. Cobb test.

Machine Furnish on 60g/m^2 Wove grade		
Fibrous	Chemithermal mechanical pulp	50%
-	White Offcuts	17%
-	White Letter Waste	17%
	White Waste Rejects	8%
	Own Broke	8%

Chemicals

Retention Aid - Cationic Polyacrylamide Nalfloc 4662 commercially available from Nalco Ltd.

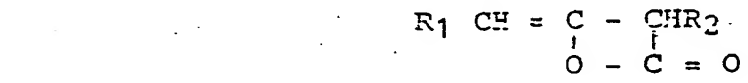
Fillers - Calcium carbonate addition to a specified sheet ash of 23% w.o.f.

Size Type	Size Addition % as Received	Retention Acid Addition g/tonne	% Sheet Ash	Sizing/mm Cobb Oven Cured 3 min at 105° C
Aquapel C348	3.7	257	23.4	17.7
Composition(1)	1.6	257	22.9	16.9

These results are averaged over a period of 5 hours of continuous machine operation.

Claims

1. An active sizing composition comprising an aqueous emulsion of a reactive sizing agent and an anionic dispersant and/or emulsifier serving to stabilise the emulsion, the reactive sizing agent comprising at least one compound according to the formula



wherein R_1 and R_2, which may be the same or different, are hydrocarbon radicals each having at least six carbon atoms.

2. A sizing composition according to claim 1, in which R_1 and R_2 are, independently of each other, alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkaryl radicals.

3. A sizing composition according to claim 2, in which R_1 and R_2 are, independently of each other, C_{12} to C_{22} alkyl groups.

4. A sizing composition according to any preceding claim, in which te anionic dispersant or emulsifier comprises one or more of sodium lignosulphonate, calcium lignosulphonate and the sodium salt of the naphthalene sulphonic acid.

5. A sizing composition according to any preceding claim, in which the dispersant or emuslifier is present in an amount of 0.5% to 10% based on the weight of the reactive sizing agent.

6. A sizing composition according to any preceding claim, including at least one substance wich extends or modifies the anionic charge density of the composition.

7. A sizing compositions according to claim 6, in which the extender or modifier comprises one or more anionic polyacrylamides, anionic starch or colloidal silica.

8. A sizing composition according to any preceding claim, containing reactive sizing agent in an amount of 5% to 20% by weight of the composition.

9. A sizing composition according to claim 8, in which the amount is 10% to 15% by weight of the composition.

10. A method of sizing paper, using a composition according to any preceding claim.

11. A method according to claim 10, in which the sizing is carried out in the presence of a cationically charged substance.

12. A method according to claim 11, in which the cationically charged substance is a filler or a retention aid.

13. A method according to claim 10, in which the sizing is carried out in the presence of a fluorescent whitening agent.

14. A method according to any of claims 10 to 13, which is carried out at the wet end of a paper making process.

15. Sized paper made by a method according to any of claims 10 to 14.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 9876

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 861 376 (D.W.EDWARDS ET AL) * claims 1-16 *	1-5,8-12, 14-15	D 21 H 17/17 D 21 H 17/23

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	14 December 90	FOUQUIER J.P.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
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P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
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